CHARACTERIZATION STUDIES OF HIGH CAPACITY COMPOSITE ELECTRODE STRUCTURES

MICHAEL. M. THACKERAY (PI)

Chemical Sciences and Engineering Division
Argonne National Laboratory

JASON. R. CROY (CO-PI)

Chemical Sciences and Engineering Division
Argonne National Laboratory

Annual Merit Review
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Project ID # BAT235

Overview

Timeline

- Start date: FY16
- End date: FY18
- Percent complete: 100%

Budget

- Total project funding
  - 100% DOE
- Funding for FY17
  - $500K

Barriers

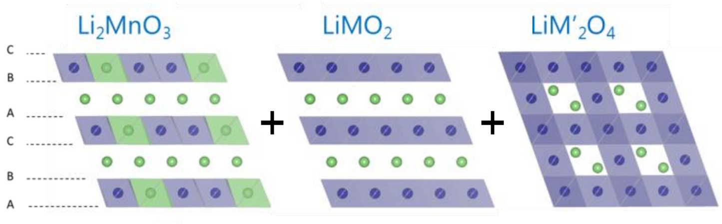
- Low energy density
- Cost
- Abuse tolerance limitations

Partners

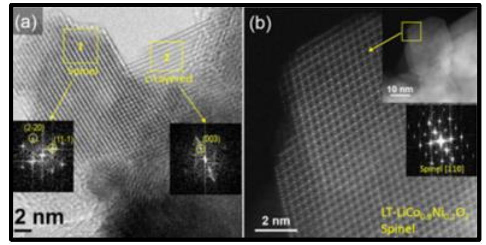
- Lead PI: Michael Thackeray, Co-PI: Jason R. Croy
- Collaborators:
  - CSE, Argonne: Eungje Lee, Arturo Gutierrez, *Meinan He*, Roy Benedek, Fulya Dogan Key (NMR), Soojeong Kim (XAS)
  - APS, Argonne: Yang Ren (XRD)
  - Pohang Accelerator Lab (Korea): Docheon Ahn (X-ray)
  - PNNL: Chongmin Wang (TEM)
  - NUANCE, Northwestern University: Vinayak Dravid, Jinsong Wu (TEM)
  - Northwestern University: Christopher Wolverton (Theory)
  - Industry: Argonne licensees and collaborators

Relevance

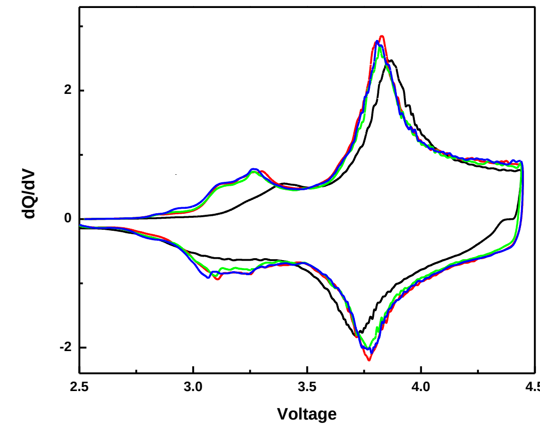
Composite Cathode Design Space



Characterization Challenges



Complex Electrochemical Properties



- Li- and Mn-rich, composite cathodes have shown promise as next-generation, high-capacity cathodes where alternatives to Co and Ni-based electrodes are desirable in terms of cost and safety
- Engineering of the nano-domains that form in these compositions, particularly in the form of “spinel-type” configuration, to create three-component, layered-layered-spinel cathodes has proven to improve rate, efficiency, and capacity with respect to pure layered-layered materials
- The complex structures and correlated electrochemical properties that result require a detailed knowledge of the relationships between composition, synthesis, final structures, and electrochemical properties in order for the rational design of improved electrode materials of this class

Milestones

- Characterize bulk and surface properties of structurally-integrated electrode materials using DOE's User Facilities at Argonne and facilities elsewhere, e.g., the spallation neutron source at Oak Ridge National Laboratory (SNS), The Environmental Molecular Sciences Laboratory at Pacific Northwest National Laboratory, and the NUANCE characterization center at Northwestern University. **Achieved/Ongoing.**
- Use complementary theoretical approaches to further the understanding of the structural and electrochemical properties of layered-spinel electrodes and protective surface layers. **Achieved/Ongoing.**
- Analysis, interpretation, and dissemination of collected data for publication and presentation. **Achieved/Ongoing.**

Approach

- A wide array of characterization techniques including X-ray and neutron diffraction, X-ray absorption, and scattering, high resolution transmission electron microscopy, MAS-NMR, and theory will be brought together to focus on challenging experimental problems. Combined, these resources promise an unparalleled look into the structural, electrochemical and chemical mechanisms at play in novel, complex electrode/electrolyte systems being explored at ANL.

- Efforts will be focused on composite layered-layered, layered-layered-spinel, and endmember components in order to inform and accelerate the design of high-energy, composite cathode materials.

- Characterization and theoretical understanding of spinel components will be pursued in order to facilitate integration of rationally-designed spinel components into layered-layered structures.

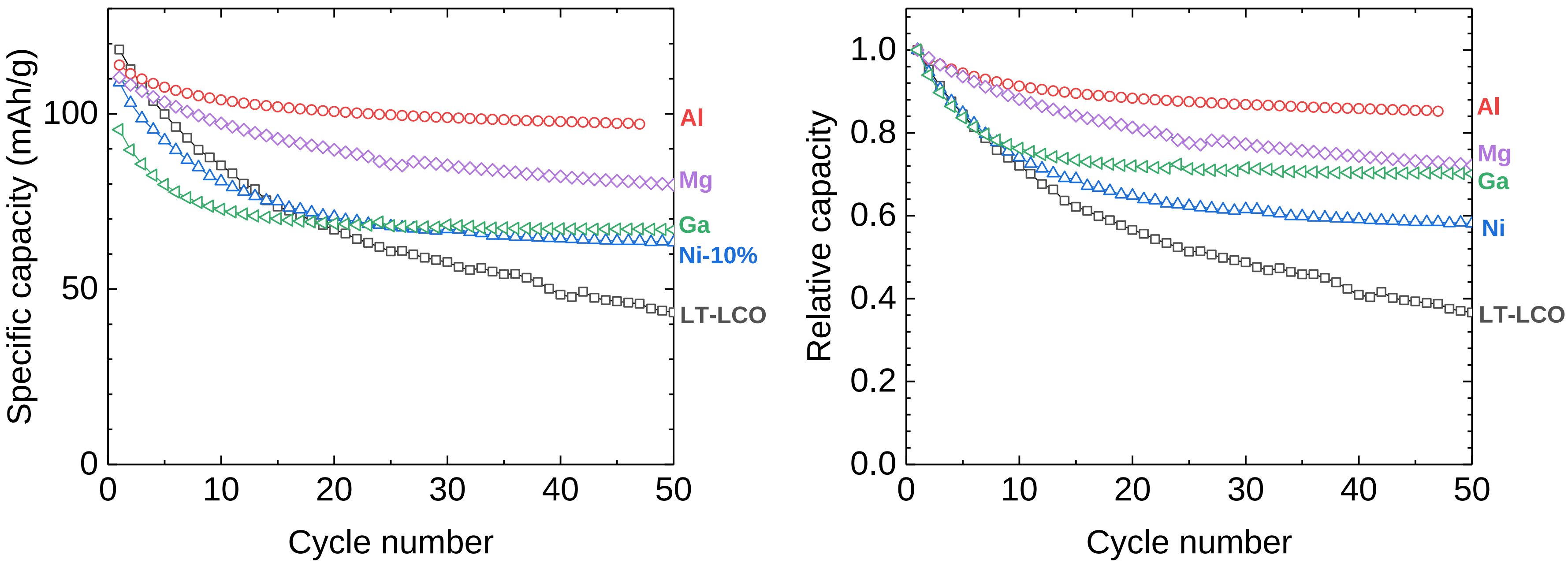
Progress: Cation substituted LT-LCO spinel

- Cation substitution for Co and associated synthesis parameters have been explored leading to the establishment of ***composition-synthesis-structure-performance*** relationships

Substituent	Effective substitution level	Effects
Mn	-	• Li_2MnO_3 and/or $Li_4Mn_5O_{12}$ formation
Ni	< 0.2	• Spinel phase stabilization
Mg	< 0.2	• Spinel phase stabilization • Good cycle stability
Ga	< 0.2	• Spinel phase stabilization • Modified Li intercalation energetics
Al	**< 0.5**	• **Spinel phase stabilization** • **Modified Li intercalation energetics** • **Excellent cycle stability**

Al-sub shows the best performance enhancements for substituted spinel phases

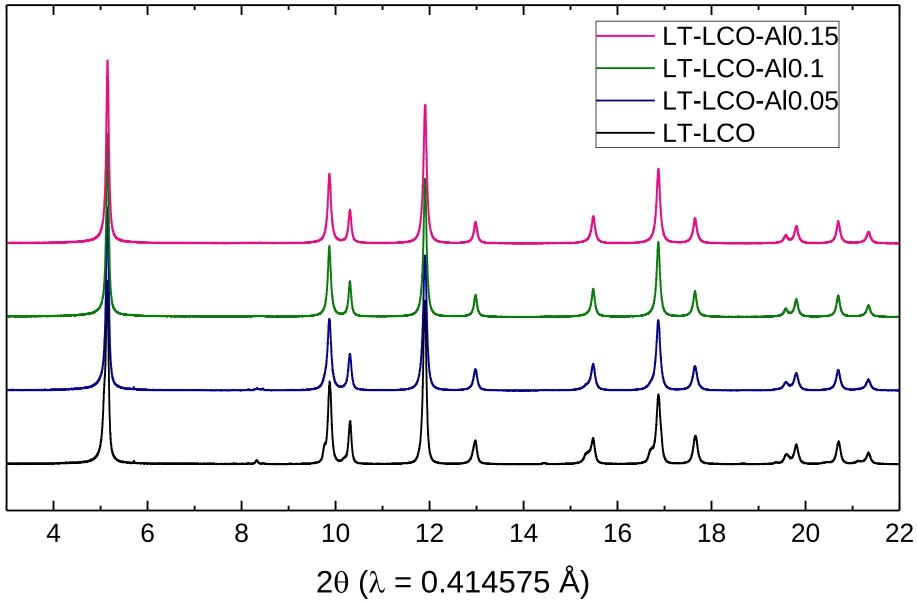
Progress: Cation substituted LT-LCO spinel

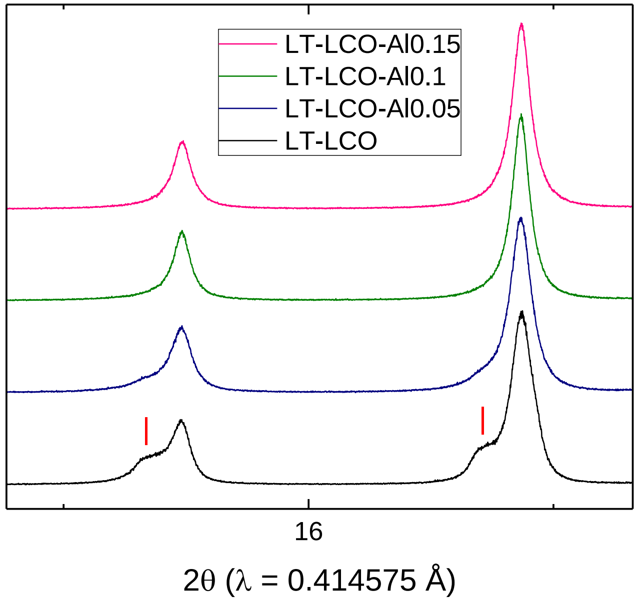


Comparison of the cycle performances of the LT-$LiCo_{1-x}M_xO_2$ cells
(M = Ni, Mg, Al, or Ga; V = 2.5 – 4.2 V; i = 15 mA/g)

- Cation M-substitution (M = Ni, Mg, Al, or Ga) stabilizes pure spinel phase by *suppressing Li/Co layer ordering at low temperature*
- Ga- or Al-substitution modifies the Li intercalation energetics as indicated by the development of sloping voltage profiles
- **Al-substitution is the most effective in enhancing the cycle stability**

Progress: Al-substituted LT-LCO spinel

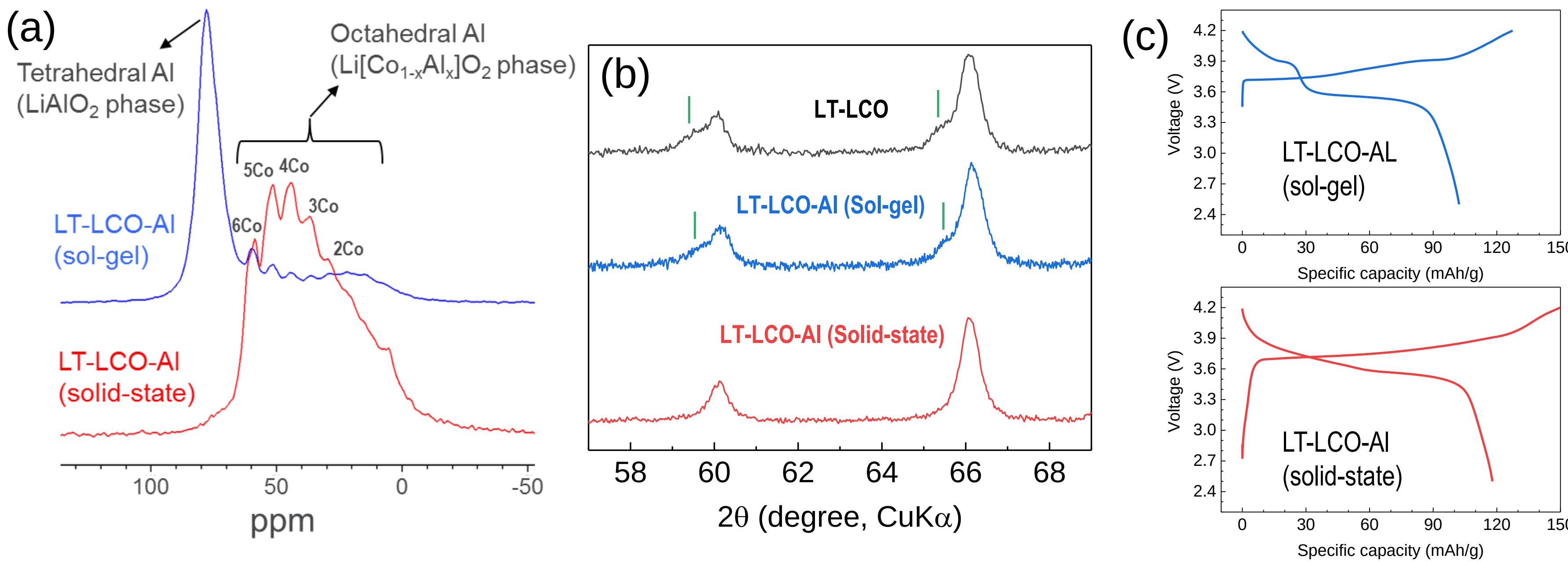




Synchrotron high-resolution XRD (HRXRD) patterns of the Al-substituted LT-LCO powder samples: While overall patterns correspond to lithiated spinel structure, pristine LT-LCO contains minor layered structure that is formed as a result of premature Li/Co layered ordering. (Peaks for the layered phase are indicated with vertical bars in the figure).

- The layered phase disappears even with 5% of Al substitution and the spinel single phase is stabilized
- No clear impurity phase is found up to 50% of Al substitution
- Lattice parameter change with Al substitution is negligible ($r_{Al(III)}$ = 53.5 pm, $r_{Co(III)}$ = 54.5 pm)

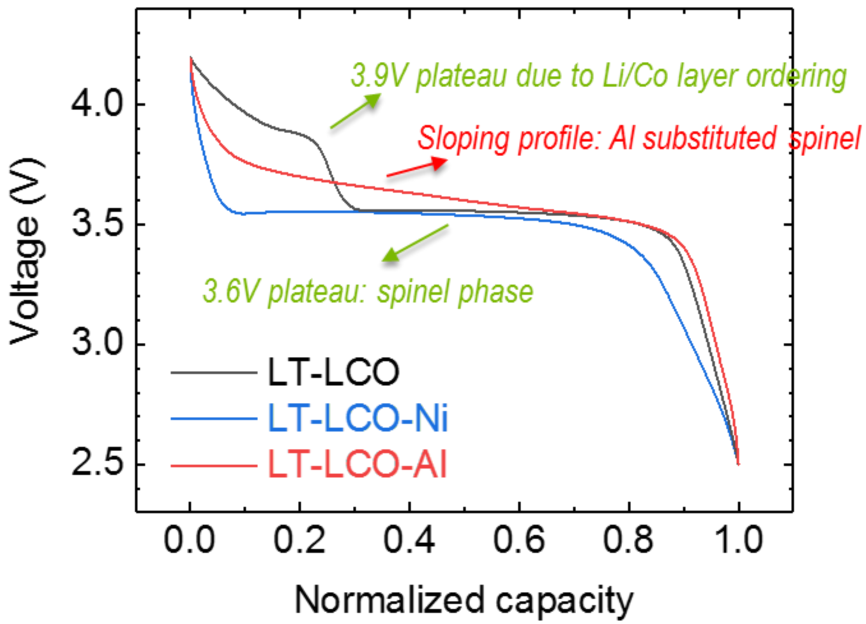
Progress: Al-substituted LT-LCO-spinel



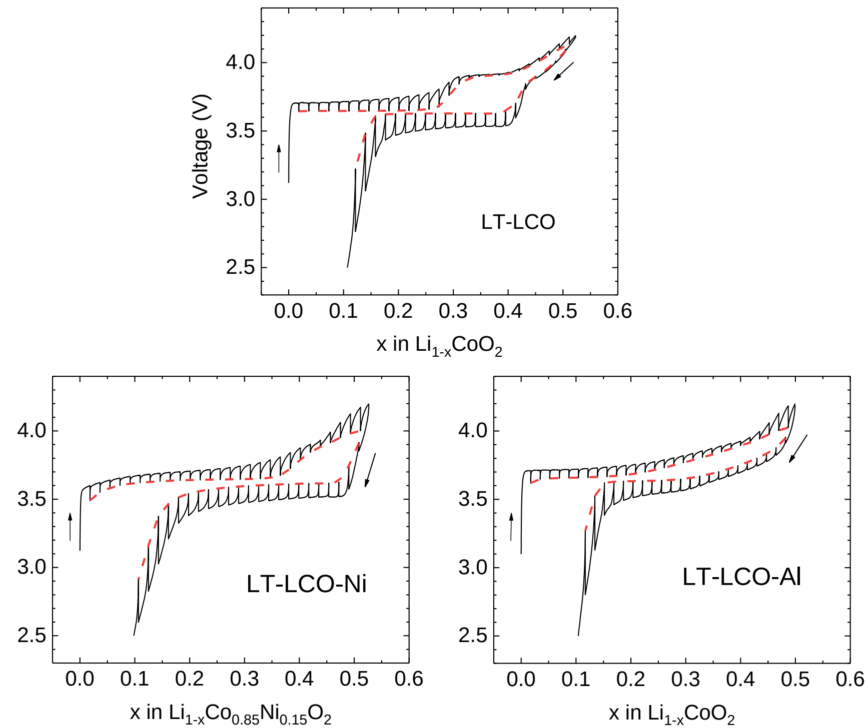
Synthesis dependency on the effective Al incorporation into bulk spinel lattice and its effect on the phase purity and electrochemistry: (a) ^{27}Al MAS NMR spectra, (b) XRD, and (c) initial charge-discharge profiles of LT-LCO-Al prepared by sol-gel or solid-state routes.

- ^{27}Al MAS-NMR confirms **effective Al incorporation into the bulk spinel lattice** of LT-LCO-Al sample prepared by solid-state synthesis route
- In contrast, for LT-LCO-Al prepared by sol-gel method, Al ions are mostly located in tetrahedral sites, presumably forming a separate $LiAlO_2$ phase
- Al incorporation promotes (1) stabilization of single-phase spinel and (2) modification of electrochemical responses

Progress: Al-substituted LT-LCO-spinel



Comparison of voltage profiles for the pristine, Ni-, and Al-substituted LT-LCO

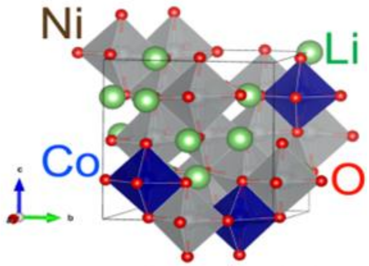


Pseudo-OCV curves of the pristine, Ni-, and Al-substituted LT-LCO

- In comparison with the Ni-substitution, which serves to reduce the amount of layered structure without changing lithium intercalation mechanisms, Al-substitution further modifies the lithium intercalation energetics as manifested in the development of sloping voltage profiles

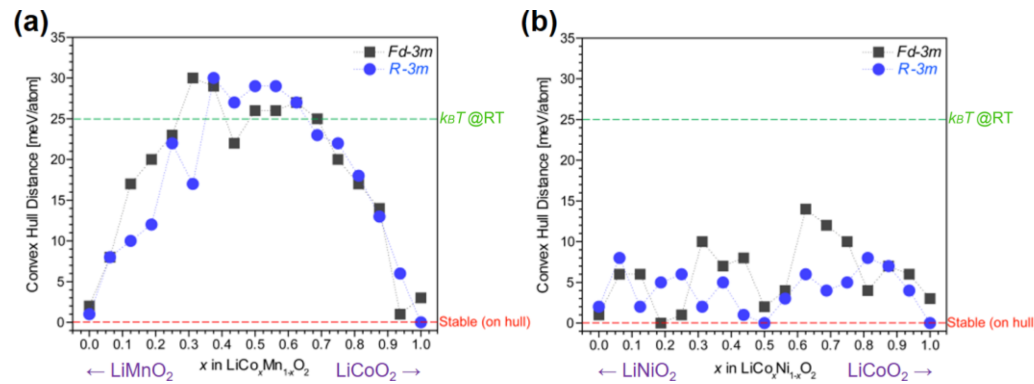
Progress: Prediction of new $LiCo_{1-x}M_xO_2$ spinel phase (M = Ni, Mn)

- A stable $LiCo_{0.1875}Ni_{0.8125}O_2$ phase (Fd-3m) is predicted by investigating the thermodynamic stabilities of all $LiCo_{1-x}M_xO_2$ (M = Ni or Mn) compounds against all other known phases in the quaternary space currently in the Open Quantum Materials Database (OQMD)

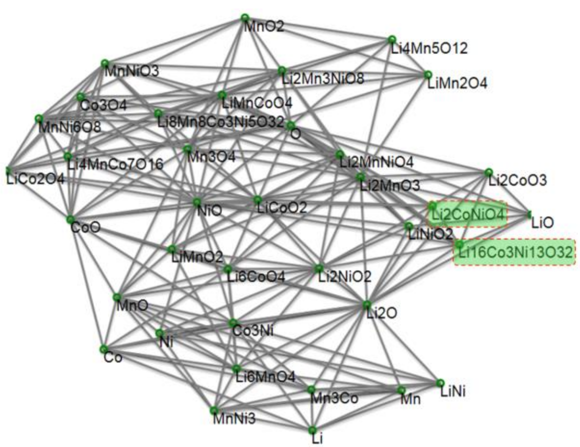


a = b = c ≈ 8.2
α = β = λ = 90°

Crystal structure of $LiCo_{0.1875}Ni_{0.8125}O_2$



Convex hull analysis of Fd-3m and R-3m $LiCo_xM_{1-x}O_2$ ($0 \le x \le 1$) for (a) M = Mn and (b) M = Ni, where stable (i.e., on the hull) and nearly stable (i.e., within 25 meV/atom of the hull corresponding to kBT at room temperature) compounds are identified.



A graphic representation of the Li-Co-Mn-Ni-O convex hull, where a green circle represents a stable compound, and every line corresponds to a two-phase equilibrium. The calculations predict $LiCo_{0.5}Ni_{0.5}O_2$ (R-3m) and $LiCo_{0.1875}Ni_{0.8125}O_2$ (Fd-3m) cathode materials, highlighted in green-colored boxes, to be stable.

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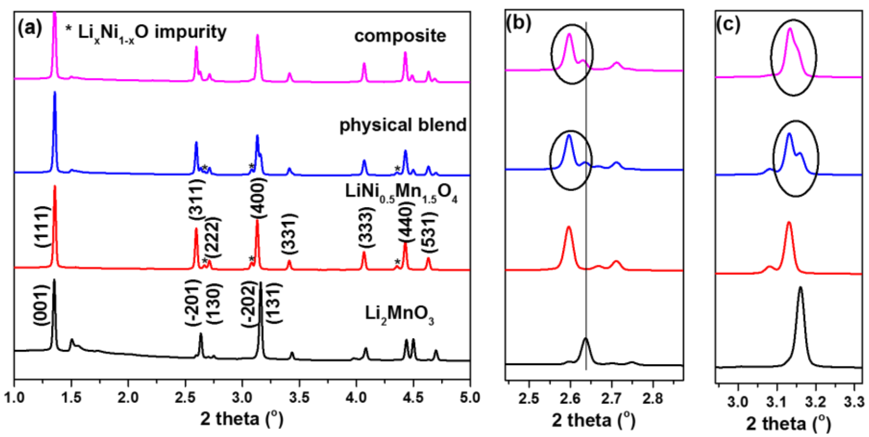
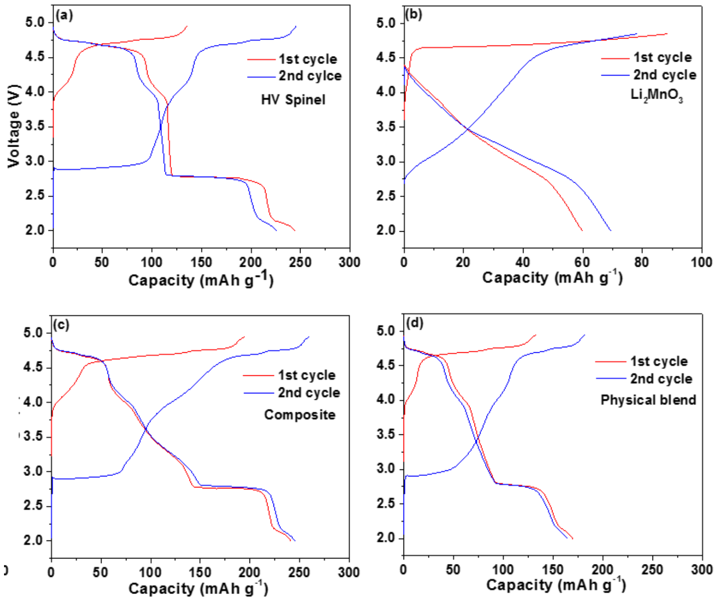
Progress: Integration of spinel

- The synthesis of multi-element composite materials requires more precise control over compositional and structural arrangements at the nano-scale
- A modified sol-gel synthesis route is applied to prepare a layered-spinel (L-S) $Li_2MnO_3 \cdot LiNi_{0.5}Mn_{1.5}O_4$ composite structure in which a heterogeneous distribution of Ni and Mn in the component phases is required
- Superior electrochemical performance of sol-gel L-S composite, in comparison with blended composite, highlights the importance of atomic scale integration of each structural component



Synchrotron XRD of Li_2MnO_3, $LiNi_{0.5}Mn_{1.5}O_4$, a 1:1 physical blend of the two, and a $Li_2MnO_3 \cdot LiNi_{0.5}Mn_{1.5}O_4$ composite.



Initial voltage profiles of (a) spinel $LiNi_{0.5}Mn_{1.5}O_4$, (b) layered Li_2MnO_3, (c) a $Li_2MnO_3 \cdot LiNi_{0.5}Mn_{1.5}O_4$ composite, and (d) a 1:1 physical blend of the two components.

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Progress: Characterization of L-L-S composite

- Systematic structural study of L-L-S composite systems is conducted by Rietveld refinements of synchrotron high-resolution X-ray diffraction (HRXRD) and neutron diffraction (ND) data
- Highlights the compositional range that stabilizes nano-scale spinel domains without decomposing the parent, layered structure

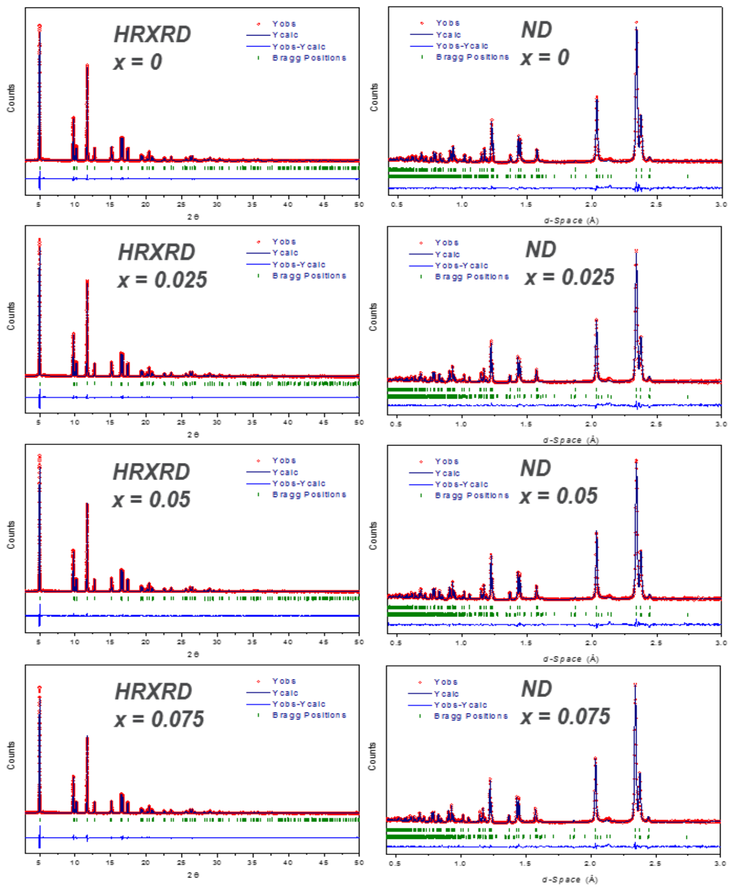
$(1-x)[0.25Li_2MnO_3 \cdot 0.75Li(Ni_{0.375}Mn_{0.375}Co_{0.5})O_2] \cdot x[Li_{0.5}Ni_{0.281}Mn_{0.531}Co_{0.187}O_2]$

Sample	*Nominal spinel content, x*	*Li/M ratio*	*HRXRD*	*ND*
A	0	1.25	R-3m	R-3m & C2/m
B	0.025	1.23	R-3m	R-3m & C2/m
C	0.05	1.21	R-3m	R-3m & C2/m
D	0.075	1.19	R-3m	R-3m & C2/m
E	0.1	1.17	Two R-3m	-
F	0.15	1.13	Two R-3m	-
G	0.25	1.06	Two-R-3m and Co_3O_4	-

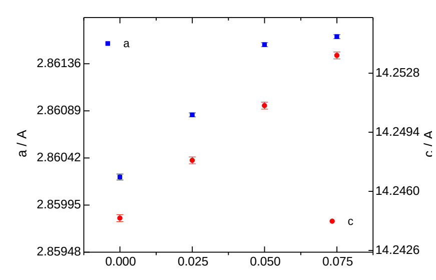
Progress: Characterization of L-L-S composite

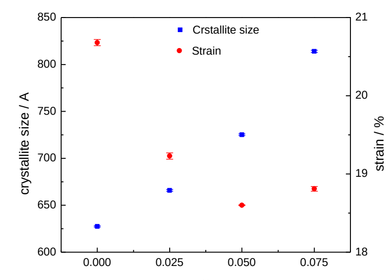
- For x = 0.0-0.075, the L-L composite model successfully fits the HRXRD (single R-3m) and ND (R3-m & C2/m) data
- Despite microscopic verification (HRTEM), *spinel* as a separate phase is not identified in HRXRD and ND, likely due to the small size and/or imperfect nano-scale spinel domains

$(1-x)[0.25Li_2MnO_3 \cdot 0.75Li(Ni_{0.375}Mn_{0.375}Co_{0.5})O_2] \cdot x[Li_{0.5}Ni_{0.281}Mn_{0.531}Co_{0.187}O_2]$



	x = 0	x = 0.025	x = 0.05	x = 0.075
Li at 3b site (%)	92.57	92.07	91.96	92.26
Ni at 3b site (%)	**6.78**	**6.73**	**6.80**	**6.41**
Mn at 3b site (%)	**0.32**	**0.91**	**1.04**	**1.13**
Co at 3b site (%)	**0.32**	**0.29**	**0.19**	**0.20**
Mn at 3a site (%)	37.18	36.59	36.46	36.37
Co at 3a site (%)	24.68	24.71	24.81	23.8
Ni at 3a site (%)	30.72	30.77	30.7	31.09
Li at 3a site (%)	**6.78**	**6.73**	**6.80**	**6.41**
Reliability (R_p, R_{wp}, R_{exp})	4.75, 4.94, 2.04	5.30, 5.44, 2.14	5.03, 5.44, 2.12	5.23, 6.06, 2.12





Lattice volume increases and lattice strain decreases as the nominal spinel content, x increases.

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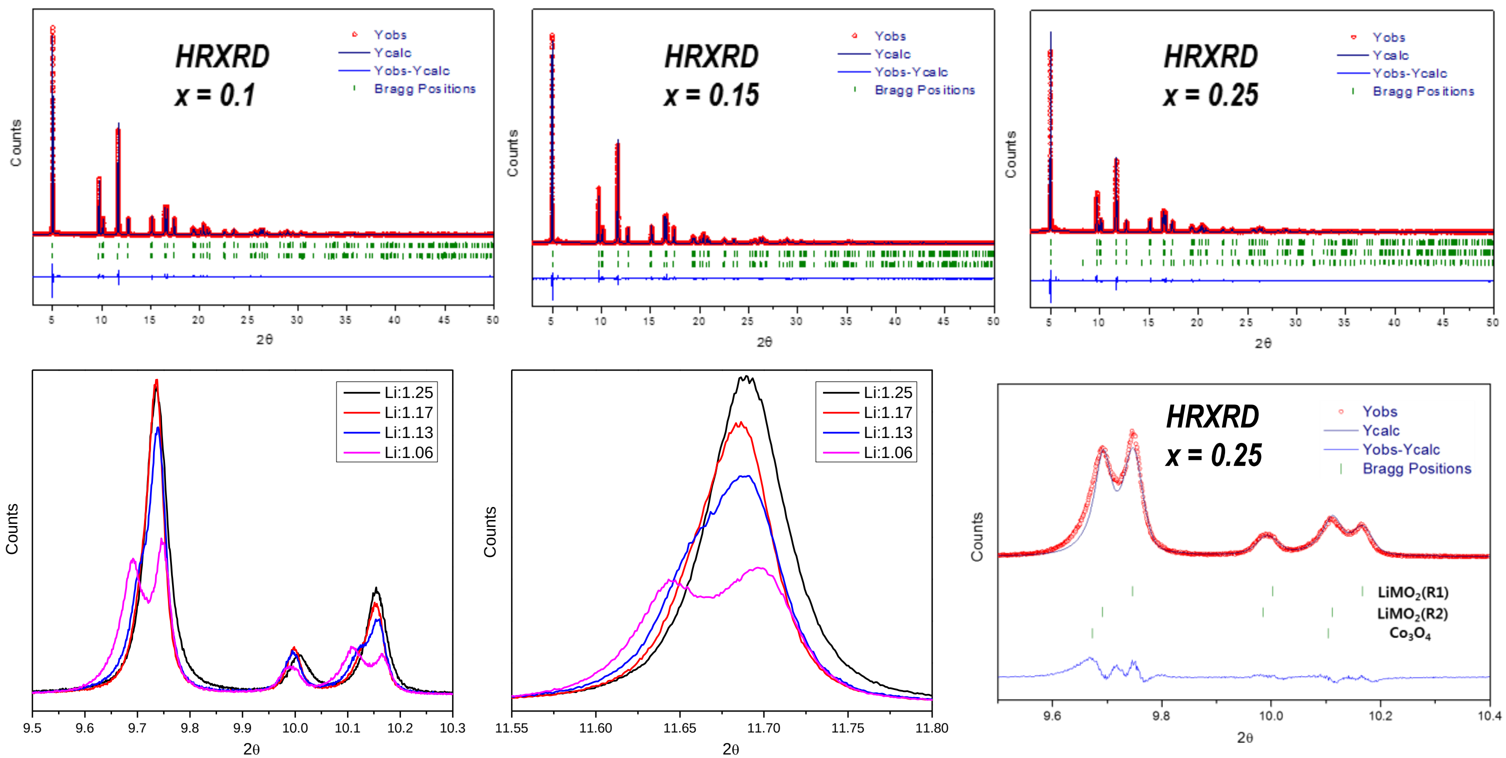
Progress: Characterization of L-L-S composite

- For $x \leq 0.1$, the parent layered phase decomposes into two layered phases with different unit cell parameters

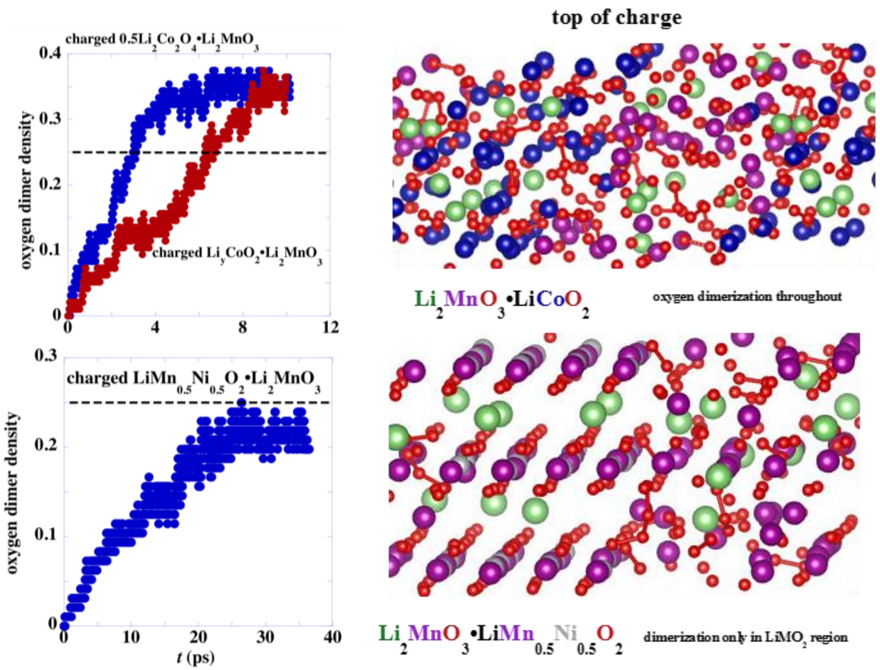
- Rietveld refinements were performed successfully with more than the two phases:
  - *$x = 0.1$: $LiMO_2$ (R-3m) & $LiMO_2$ (R-3m)*
  - *$x = 0.15$: $LiMO_2$ (R-3m) & $LiMO_2$ (R-3m)*
  - *$x = 0.25$: $LiMO_2$ (R-3m) & $LiMO_2$ (R-3m) & Co_3O_4*

$(1\text{-}x)[0.25Li_2MnO_3 \cdot 0.75Li(Ni_{0.375}Mn_{0.375}Co_{0.5})O_2] \cdot x[Li_{0.5}Ni_{0.281}Mn_{0.531}Co_{0.187}O_2]$

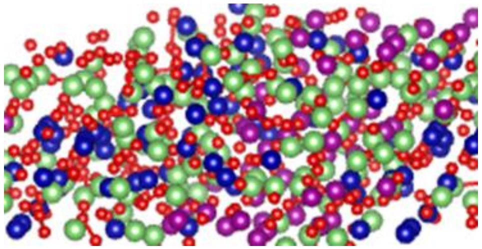


Progress: Modeling of Li- and Mn-rich type cathodes

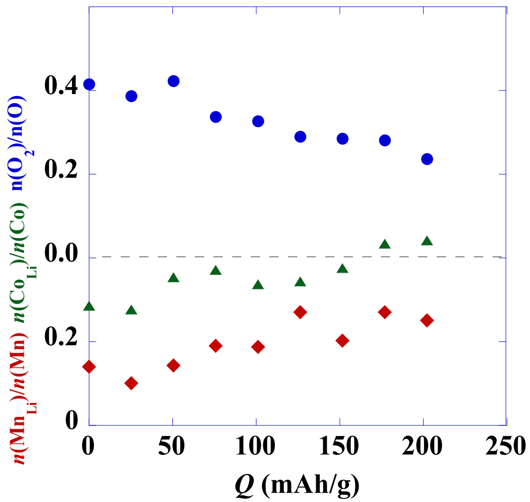
- Simulations show that the structural damage on the layered-layered composite cathode during the initial activation process has minimal reversibility
- Suggestions for stable operation of Li- and Mn-rich type cathodes:
  - Restrict charge to half of the initial activation plateau (~200 mAh/g)
  - Apply semi-coherent coating to stabilize surface oxygen



Structural transformation of Li- and Mn-rich cathode at the top of charge step: Crystalline structure is mostly damaged during the initial activation process via oxygen dimerization and transition metal migration



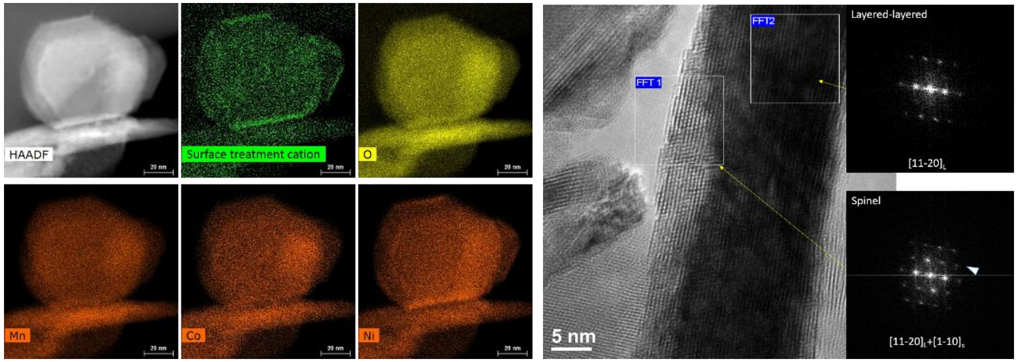
Discharge process dissociates only about half of the oxygen dimers, and little transition metal migration occurs



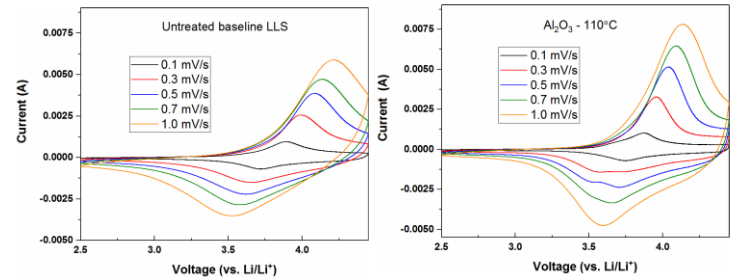
Bader charge analyses indicates that the charge compensation during the initial discharge takes place by O, Co reduction.

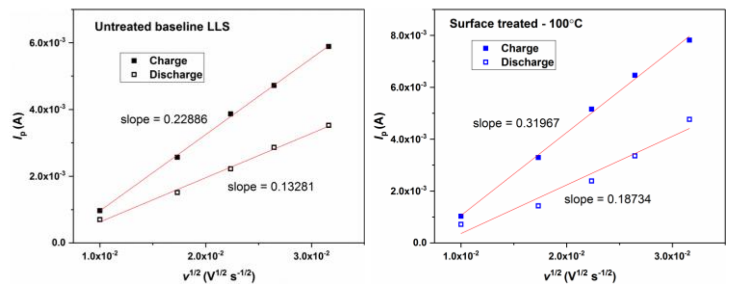
See also BAT049

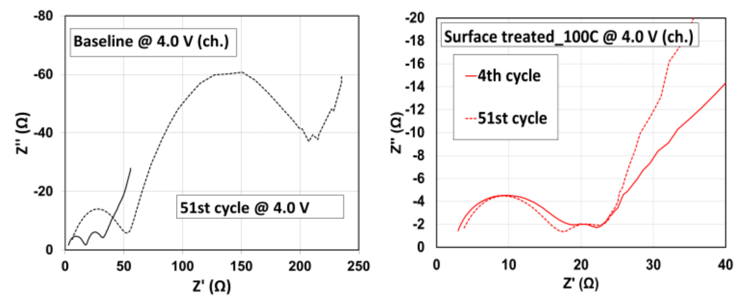
Progress: Surface treatment and electrolyte additives



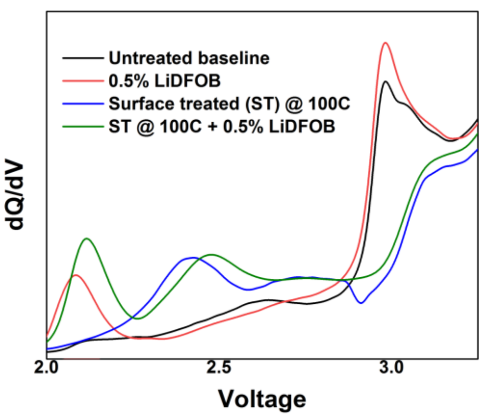
Surface-treatment cation is evenly distributed throughout the whole particle surface. Spinel structure is observed on the surface of the surface-treated L-L-S cathode particles







Surface treatment improves electrode kinetics and stability



dQ/dV plots of the first formation cycles of LLS//Gr full cells with and without Al surface treatment and LiDFOB additives

- **Synergistic performance improvement** by low-temp Al surface treatment and electrolyte additives (e.g., LiDFOB) is confirmed in L-L-S//Gr full cells

Response to Previous Year Reviewer Comments

General Comments

- The reviewer praised the approach taken as excellent. It proceeds in a logical manner. A wide array of characterization techniques… will be used to gain a better understanding of the challenges confronting the next generation of electrode materials.
- …High specific energy cathode materials with reduced cost and improved safety are required to address shortcomings. The LLS composite cathodes with suitable surface coatings are promising to provide stable structures, with high capacities at high rates and are being addressed in this project. This project is thus highly relevant to the DOE goals.
- The reviewer said nice work, and liked that the work is focusing on more than just voltage fade, but other problems that need to be addressed as well. There is good work on scale up, but lots of work. It is an ambitious effort that seems to be going well.

Response

- We thank the reviewers for their time and encouraging comments concerning our manganese-rich cathode work and the progress being made.

Response to Previous Year Reviewer Comments

General Concerns

- Extreme local information (e.g., HRTEM and XRD, although those are in very high qualities and good references), should not be directly correlated to the electrochemical performance data because performance data reflect the ensemble of the material in the electrode including amorphous phases and even impurities.

Response

- One of the main objectives of this project is to ascertain the exact nature and role of the local structures that form within these materials. It has been shown and reported on several times in the literature (and by the PIs) that it is, in fact, the local atomic arrangements that form in these materials that give them their unique properties. In addition, we now know from several studies that defects, even in small concentrations, can help to define the observable, macroscopic, electrochemical character of these cathodes. While the reviewer is correct that performance data represents the average of all contributions from the material, small modifications to the phases and local structures present can alter the materials performance. It is the goal of this project to understand the synthesis and characterization of those alterations and their influence on performance.

Response to Previous Year Reviewer Comments

General Concerns

- It is also important to demonstrate the benefits of these LLS cathode materials with surface coatings in an industrial environment in comparison with the surface-treated NCA-based cathode to properly address the technical barriers in the VTO program.

Response

- We agree with the reviewer that industrial validation in practical cells is of critical importance for any cathode technology. However, the main focus of this program is synthesis and characterization of domain structures and their associated affect on electrochemical properties. In addition, any cathode technology incorporating Co, even in small amounts such as NCA, or high nickel such as NMC-811, will face challenges in terms of cost and safety, as well as politics. As such, development of competitive alternatives will be essential if the lithium-ion market continues to grow as predicted.

Response to Previous Year Reviewer Comments

General Concerns

- The reviewer expressed anticipation about the results for all 40 compositions and hoped this can be completed in the time remaining. The reviewer also wanted to see more detail about how much characterization and testing were being planned for the other compositions.

Response

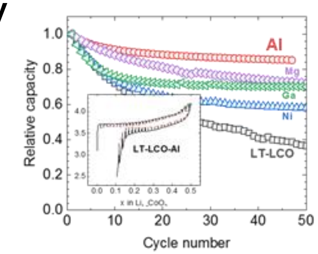
- Unfortunately, this project did not receive funding in FY18 due to budget uncertainties. As such, our characterization and analysis of these compositions was not possible and many of them will have to be re-synthesized if future studies are to be made.

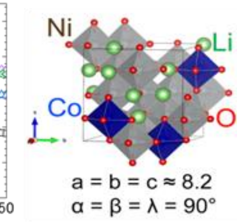
Proposed Future Research

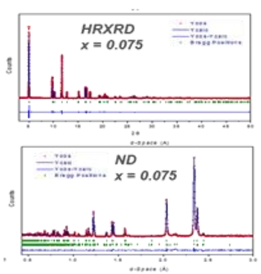
- ***This project is no longer funded***

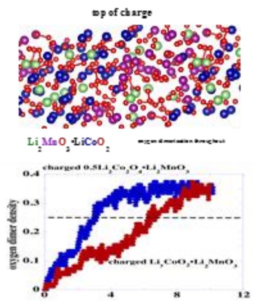
Summary

- Cycling stability of Co-based spinel compounds is greatly improved by cation substitution (particularly aluminum) and precise synthesis control approaches. DFT calculations unravel their unique lithium intercalation mechanisms and predict new stable spinel compounds.



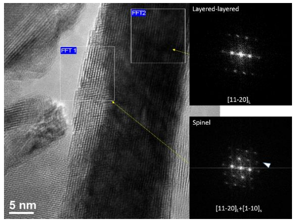


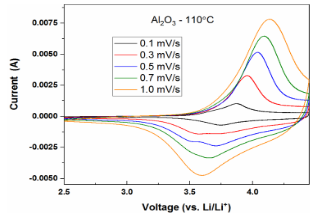




- Systematic structural characterization using synchrotron X-ray techniques, neutron diffraction, and high resolution electron microscopy reveals that the critical role of the ‘spinel’ component in improving the layered-layered-spinel (LLS) composite cathodes can be optimized when the spinel is atomically embedded as a nano-scale domain.

- Full cell performances of LLS cathodes are significantly improved by surface treatment and electrolyte additives. The protection of the particle surface by chemical species such as Al and nano-scale spinel domains are revealed by electrochemical characterization, high resolution imaging, and spectroscopy techniques.





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Remaining Challenges and Barriers

- Significant concerns with high-energy, NMC-based, lithium-ion batteries are cost and safety. Not only with respect to Co in terms of cost, but safety with respect to nickel-rich NMCs; which may also become cost prohibitive depending on increased demand. Mn-rich alternatives to Ni/Co-based NMCs provide promising options for safe, high-energy batteries. The concept of layered-layered-spinel materials has shown steady progress in terms of efficiency, rate, capacity, and surface stability. Critical challenges going forward will include:

  - Further improvements to our understanding and enhancement of structural stability
  - Development of advanced synthesis of engineered surface structures
  - Detailed understanding of impedance in LLS materials
  - Testing and analysis of large cell formats